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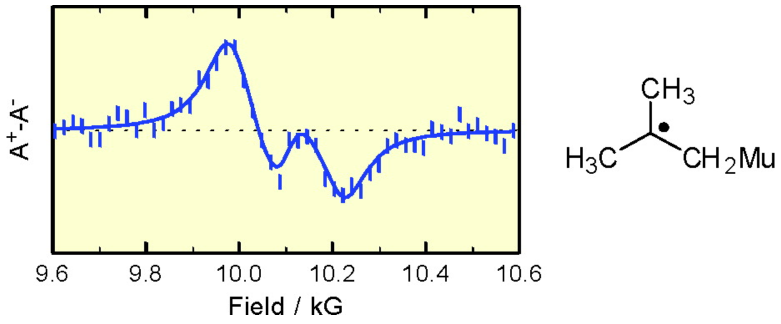
J. Am. Chem. Soc., **2005**, 127 (39), 13714-13719• DOI: 10.1021/ja0537070 • Publication Date (Web): 07 September 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Published on Web 09/07/2005

Organic Free Radicals in Superheated Water Studied by Muon Spin Spectroscopy

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Abstract: There is a pressing need to identify and monitor reaction intermediates in water at high temperatures and pressures, but conventional techniques have limited capability for studying transient free radicals under such challenging conditions. Apparatus has now been developed to permit muon avoided-level crossing spectroscopy (μLCR) of organic free radicals in superheated water. The combination of μLCR with transverse-field muon spin rotation (TF-μSR) provides the means to identify and characterize free radicals via their nuclear hyperfine coupling constants. Because the radicals are derived from the addition of muonium (Mu = μ^+e^-) to unsaturated compounds, the ensuing muoniated free radicals correspond to conventional organic free radicals but with a muon spin label substituted for one of the protons. Muon spin spectroscopy is the only technique presently being used to characterize transient free radicals under hydrothermal conditions in an unambiguous manner, free from interference from other reaction intermediates. This paper demonstrates how muoniated radicals can be used to monitor the species present in hydrothermal systems, and examples are presented from two classes of reaction: dehydration of alcohols and enolization of ketones. Spectra are displayed and hyperfine constants reported for muoniated forms of the following free radicals in superheated water (typically 350 °C at 250 bar): 2-propyl, 2-methyl-2-propyl (*tert*-butyl), and 2-hydroxy-2-propyl. The latter radical is the product of muonium addition to both the keto and the enol forms of acetone, but different isotopomers are produced according to which reaction channel is dominant. This should prove invaluable in future studies of the role of enols in combustion.

Introduction

Research on organic chemistry under hydrothermal conditions is motivated by a remarkable diversity of applications: geochemical production of fossil fuels, biology of submarine volcanic vents, corrosion in pressurized water nuclear reactors, destruction of chemical weapons and other hazardous materials, and new industrial processes whose development is spurred by the trend toward "green" chemistry.[1,2] However, fundamental investigations of chemical reactions require the detection and monitoring of intermediates,[1] often transient free radicals, and there has been a significant technological barrier to progress in this direction.

Organic free radicals are best characterized by electron spin resonance (ESR) and associated forms of magnetic resonance spectroscopy, because the existence of an ESR signal gives unambiguous proof of a radical, and the hyperfine structure of the spectrum provides nuclear hyperfine coupling constants, which can be used to identify the species. However, although application of ESR has been successfully demonstrated for both stable and transient radicals in organic supercritical solvents,[3] such experiments are technically demanding and restricted in their application. Furthermore, the high critical constants of water, the strong dependence of its dielectric constant on temperature, and the corrosive nature of superheated water impose additional difficulties, and to date there has been no report of ESR studies on superheated aqueous solutions. Thus, studies of transient radicals under hydrothermal conditions rely on optical spectroscopy.[4−7] These experiments are conceptually simpler than ESR, but they have their own complications, including corrosion of optical windows, critical opalescence, and variation of extinction coefficients with physical conditions.

Most of the technical difficulties that face ESR and optical studies of hydrothermal systems do not apply to muon spin

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10.1021/ja0537070 CCC: $30.25

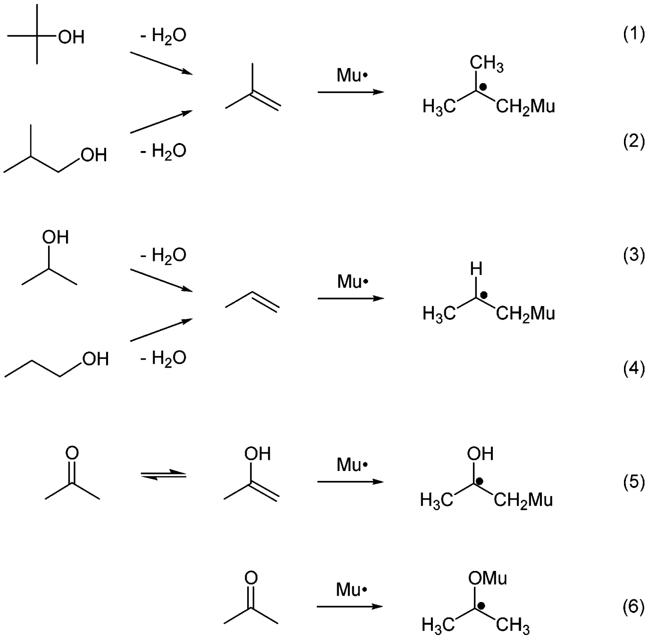
spectroscopy. Muonium, the single-electron atom with a positive muon as nucleus, behaves chemically like a hydrogen atom and can be used to probe the chemistry of H atoms and free radicals incorporating H.[8] We have already demonstrated the ability to study muonium[9] and muoniated free radicals[10] in water over a range of conditions from ambient to in excess of 400 °C and 400 bar. Our publications to date[9−12] report experiments using the transverse-field muon spin rotation technique (TF-μSR) and a spectrometer limited to moderate magnetic fields (up to 2 kG). While this apparatus is appropriate for studies of muonium[9] and Mu reaction kinetics,[11] it permits only limited studies of muoniated radicals.[10,12] In particular, it does not have the capability for muon avoided-level crossing spectroscopy (μLCR), which is necessary for full characterization of a radical, as was pointed out in our study of acetone enolization via radical formation.[12]

In this report, we describe the development of new apparatus and techniques to overcome this limitation and then demonstrate the capability to identify transient organic radicals and thereby infer the nature of their precursors in the hydrothermal medium. We explore applications in two areas: (1) dehydration of alcohols, and (2) the enolization of acetone. The first application was chosen primarily as a proof-of-principle investigation of a relatively well-understood system. However, while there was little doubt as to the identity of the radicals detected, the spectroscopic data gathered (hyperfine coupling constants) are novel. This is also true of the radicals detected in the second application, but here the incentive was to characterize the competitive products of reaction with the participants in the keto−enol equilibrium, with the eventual aim of determining the equilibrium constant. The radicals detected, and their means of generation in superheated water, are listed in Scheme 1.

Experimental Section

Experiments were carried out at the M9B muon channel of the TRIUMF cyclotron facility, in Vancouver, British Columbia. The channel was tuned to deliver muons of nominal momentum 70 MeV/c, this being just sufficient to allow the muons to penetrate the 2 mm thick titanium window of the pressure cell and come to rest in the aqueous sample. Unlike our previous μSR studies of muonium[9,11] and muoniated radicals[10,12] in superheated water, the recent work employed the HELIOS muon spectrometer, which is typically used for radical studies[13] on a low momentum beam line. Because HELIOS is based on a superconducting solenoid with axial bore, the beam of muons enters from one end and the target cell and plumbing from the other. Our old cell design[9a] is incompatible with this geometry, so new apparatus was constructed. Further details are given in the Supporting Information.

Scheme 1. Generation of Muoniated Radicals in Superheated Water



Decay muon channels, such as M9B, are normally set up to provide longitudinally spin-polarized muons. This is appropriate for μLCR, which relies on monitoring the asymmetry in muon decay by counting positrons emitted in the forward and backward directions with respect to the muon beam.[13] Longitudinal polarization is much less convenient for TF-μSR, because the magnet field must be applied transverse to the beam direction, an arrangement which leads to beam bending. In any event, high magnetic fields are only available along the axis of the HELIOS spectrometer. This is not a problem on a low momentum beam line equipped with a spin rotator. However, such a device is not practical on high momentum channels such as M9B, because to rotate the spins of fast muons to the desired amount would require unattainable electric fields. Nevertheless, a serendipitous failure of a beam line element resulted in the selection of an off-axis momentum bite and significant transverse polarization, albeit at the expense of beam intensity. Thus two different beam tunes were employed to enable both μLCR and μSR experiments on the same sample/spectrometer setup with only a minor adjustment in positron detector positions.

Muon hyperfine constants A_μ were extracted from TF-μSR spectra, usually from the difference of a pair of muon spin precession frequencies. In a few cases, where the higher frequency signal lacked sufficient signal-to-noise to give reliable results, A_μ was determined from a combination of the lower frequency (stronger) radical signal and the diamagnetic muon Larmor frequency, as described previously.[10] Proton hyperfine coupling constants A_p were determined from the field positions of resonances in μLCR spectra.[8,15] The equations used to calculate A_μ and A_p are given in the Supporting Information.

Dehydration of Alcohols

Although it seems counterintuitive, heating alcohols in water can result in dehydration[1,2,16−18] to form alkenes. The onset and

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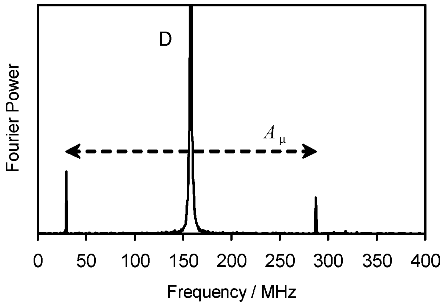

Figure 1. Fourier power μSR spectrum of the muoniated *tert*-butyl radical in water at 250 °C and 252 bar in a transverse magnetic field of 11.65 kG. The truncated peak D is due to muons in a diamagnetic environment.

extent of the reaction depends on the nature of the alcohol, and it has been established that ease of dehydration increases in the order primary, secondary, tertiary alcohols. Thus, *tert*-butyl alcohol (2-methyl-2-propanol) is known to undergo almost complete conversion to isobutene (2-methylpropene) at temperatures as low as 225 °C.[16]

Because muonium behaves chemically like a hydrogen atom, it readily adds to alkenes. It can therefore be used as a spin (and isotope) marker, to label the alkene as it is produced. This is evident from the transverse-field μSR spectrum displayed in Figure 1, which was derived from a sample of 1 M *tert*-butyl alcohol in water. Unlike our previous work,[10] in the present arrangement the magnetic field can be set sufficiently high in HELIOS that both radical frequencies are positive, equally spaced about the diamagnetic muon signal (*D*). The difference between the two radical frequencies directly gives the muon hyperfine coupling constant: 258.1 MHz. Just like the isotropic proton coupling constants derived from hyperfine splitting of ESR spectra, the muon coupling constant is sensitive to the unpaired electron spin distribution in the free radical.[8]

The diamagnetic signal arises from muons in diamagnetic environments, such as MuH and MuOH, and is characterized by a fractional muon polarization $P_D = 0.59$ at 250 °C.[9a] The amplitudes of the radical and diamagnetic precession signals were determined by fitting the μSR spectrum in the time domain. By comparing the amplitude of the lower radical frequency to that of the diamagnetic signal, we deduce that the muon polarization in the radical is $P_R = 0.16$, close to the value $P_R = 0.18$ found for muonium in pure water under the same conditions.[9a] Taking into account the expected enhancement of the diamagnetic signal due to some muon stopping in the cell wall, we deduce that all of the spin-polarized muonium is converted to free radical at a rate faster than the difference in muonium and radical precession frequencies, that is, $>10^{10}$ s^{-1}. This in turn implies that most, if not all, of the *tert*-butyl alcohol in the sample has been converted to isobutene, which is expected to react with muonium with a rate constant of about 3×10^{10} M^{-1} s^{-1}.[11] It should be noted that it takes up to 30 min to adjust the temperature and pressure of our samples, and an hour or more to acquire a TF-μSR or μLCR spectrum, so the signal amplitudes depend on the equilibrium or integrated concentration of the radical precursor.

The same sample was also investigated by μLCR under similar conditions (250 °C and 250 bar); the spectrum is displayed in Figure 2a. The characteristic shape of the signal is caused by two partially overlapping resonances[19] due to two inequivalent groups of protons and is consistent with the extrapolation of results from an earlier investigation using pure isobutene at lower temperatures.[13a] The two resonances arise from the different hyperfine constants of the protons in the CH_3 groups and the CH_2Mu group. The position of each resonance is determined primarily by the difference between the muon hyperfine constant (hfc) and the relevant proton hfc. The lower-field, more intense resonance is assigned to the unsubstituted methyl groups; the corresponding proton hfc is temperature independent, whereas the proton hfc for the CH_2Mu group rises with temperature, as found previously.[13a] A summary of the analysis is given in Table 1.

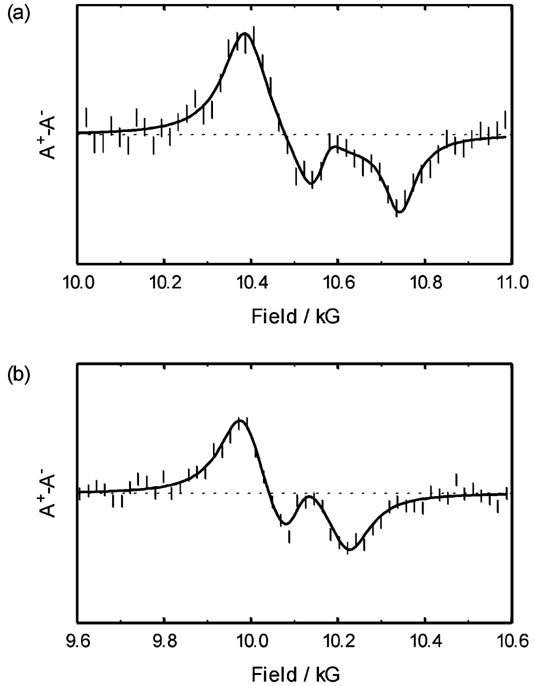

Figure 2. Muon avoided-level crossing spectra of the muoniated *tert*-butyl radical in water, derived from (a) 1 M *tert*-butyl alcohol at 250 °C, 250 bar; and (b) 0.01 M *tert*-butyl alcohol at 350 °C, 260 bar.

In a subsequent experiment using one-hundredth the concentration of *tert*-butyl alcohol, a strong μLCR spectrum was still apparent (Figure 2b), even though no radical signal could be observed in TF-μSR. This highlights one advantage of μLCR: it can be used to investigate smaller concentrations of solutes than TF-μSR, which suffers loss of signal due to spin dephasing as the muon precession rate changes from muonium to the radical product. Because μLCR involves monitoring the muon polarization parallel to the magnetic field, it is unaffected by dephasing. Consequently, the signal is observed as long as the rate of formation of the muoniated radical competes favorably with the rate of processes that take the muon out of resonance (such as muon decay and spin relaxation). Typically this occurs for precursor concentrations 3 orders of magnitude lower than for TF-μSR.[15]

The utility of the hyperfine constants in identifying radicals can be seen from the third sample listed in Table 1. The data confirm that the radical signals (Figure 3), which arise from isobutanol (2-methyl-1-propanol), can also be assigned to the *tert*-butyl radical, as expressed in reaction 2 of Scheme 1.

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(19) The differential line shape is a consequence of magnetic field modulation employed to suppress baseline drift and other sources of systematic error. Unlike the sinusoidal field modulation commonly used in ESR, square-wave modulation is used in μLCR.

Table 1. Assignments and Hyperfine Constants for Muoniated Radicals Detected in Aqueous Solutions of Organic Compounds at High Temperature

sample	radical	T/°C	P/bar	B_{LCR}/kG	A_μ/MHz	A_p/MHz	assignment
1 M *t*-BuOH	$(CH_3)_2\dot{C}CH_2Mu$	250	250	10.47	258.14	62.4	CH_3
				10.66	258.14	58.9	CH_2Mu
0.01 M *t*-BuOH	$(CH_3)_2\dot{C}CH_2Mu$	350	260	10.03	249.95	62.4	CH_3
				10.17	249.95	59.8	CH_2Mu
0.69 M *i*-BuOH	$(CH_3)_2\dot{C}CH_2Mu$	350	260	10.03	249.95	62.4	CH_3
				10.18	249.95	59.7	CH_2Mu
0.98 M 2-PrOH	$CH_3\dot{C}HCH_2Mu$	350	258	10.76	269.3	68.1	CH_3
				10.91	269.3	65.4	CH_2Mu
1.03 M 1-PrOH	$CH_3\dot{C}HCH_2Mu$	350	251	10.75	269.3	68.2	CH_3
		350	251	10.91	269.3	65.4	CH_2Mu
		350	240	17.55	269.3	−57.7	α-H

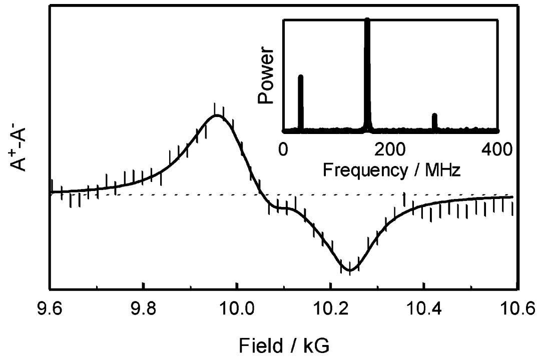

Figure 3. μLCR spectrum of the muoniated *tert*-butyl radical obtained from 0.7 M isobutanol in water at 350 °C, 250 bar. A Fourier power μSR spectrum of the same sample at 11.6 kG is shown in the inset.

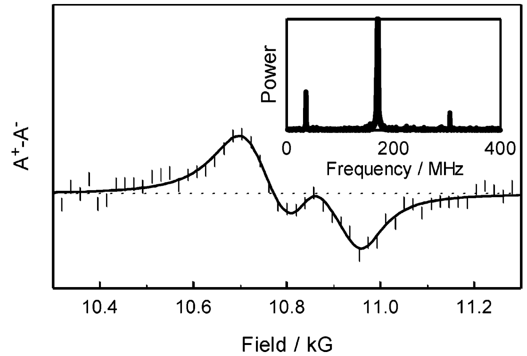

Figure 4. μLCR spectrum of the muoniated isopropyl radical obtained from 1 M 2-propanol in water at 350 °C, 250 bar. A Fourier power μSR spectrum of the same sample at 12.5 kG is shown in the inset.

Although the detection of the radical TF-μSR spectrum suggests high conversion of the alcohol to the alkene, it is significant that this only occurred after heating to 370 °C; the radical TF-μSR signal was not observed in an earlier experiment at 350 °C.

Similarly, a preliminary investigation revealed the TF-μSR signal of the 1-Mu-2-propyl radical at 350 °C from a sample of 2-propanol (Figure 4), but a sample of 1-propanol afforded only the μLCR spectrum (Figure 5). This is consistent with literature reports of the relative ease of dehydration of 1- and 2-propanol in water.[17,18] Despite the lack of a TF-μSR spectrum from 1-propanol, it is clear from the similarity of the μLCR spectra that both alcohols give rise to propene. The identity of the radical, 1-Mu-2-propyl, is confirmed by the detection of the α proton (2-H) resonance, as shown in Figure 5b. The hyperfine constants determined from these spectra are listed in Table 1.

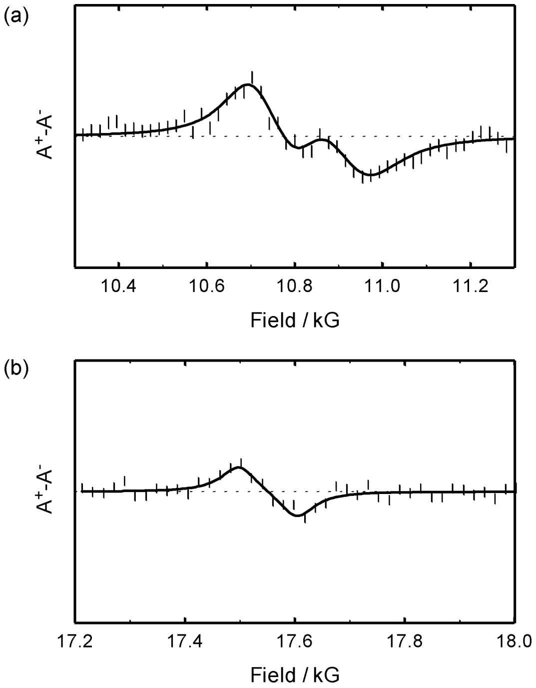

Figure 5. μLCR spectrum of the muoniated isopropyl radical derived from 1 M 1-propanol in water at 350 °C, 250 bar, showing resonances due to: (a) the CH_3 and CH_2Mu groups; and (b) the α-H.

As far as we know, there are no equivalent data on hyperfine constants of radicals containing H instead of Mu, so direct comparison is not possible. At best, we can cite literature on *tert*-butyl in isooctane at 107 °C ($A_{CH_3} = 63.6$ MHz[20]) and 2-propyl in isooctane at 79 °C ($A_{CH_3} = 68.9$ MHz, $A_H = (-)60.8$ MHz[21]).

To facilitate comparison with H data, the muon hfc's should be multiplied by 0.31413 to account for the trivial isotope effect due to the differing magnetic moments of the muon and the proton. The reduced muon coupling constants (A_μ') are still significantly higher than the unsubstituted methyl groups in the same radicals or in the isomeric H-radicals. Similarly, the proton couplings in the $-CH_2Mu$ groups are lower than those in the unsubstituted methyls. Both of these findings are consistent with a well-understood conformational effect: the light isotope (Mu) preferentially occupies the rotational site in which it eclipses the half-filled p-orbital at the radical center.[13a,14] An average hyperfine constant for the $-CH_2Mu$ group can be defined by

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Table 2. Assignments and Hyperfine Constants for Muoniated Radicals Detected in Aqueous Solutions of Acetone at Low and High Temperature

radical	T/°C	P/bar	B_{LCR}/kG	A_μ/MHz	A_p/MHz	assignment	origin
$(CH_3)_2\dot{C}OMu$	92	136	1.37	32.7	57.9	CH_3	keto
$CH_3\dot{C}OHCH_2Mu$	350	250	10.06	250.5	62.5	CH_3	enol
			10.21	250.5	59.7	CH_2Mu	enol

$(A_\mu' + 2A_{CH_2Mu})/3$ to account for the conformational preference. It still gives a value for the hyperfine constant 5% larger than that for $-CH_3$, consistent with previous findings.[13a]

The unsubstituted CH_3 groups in the muoniated radicals have similar, but somewhat smaller, hfc's than the literature data. This is probably due to the effect of out-of-plane bending at the radical center.[21] The α-H coupling constant is even more sensitive to this effect.

Enolization of Acetone

Identification of the Mu adduct of acetone under standard conditions dates back to the first detection of muoniated radicals by TF-μSR.[22] The assignment to the 2-muoxy-2-propyl radical $(CH_3)_2COMu$ was supported by μLCR studies, first of pure acetone[15] and subsequently of aqueous solutions.[23] Our recent study[12] of superheated aqueous solutions of acetone produced TF-μSR spectra consistent with an extrapolation of literature data[24] on the muon hyperfine constant, which varies with temperature and solvent. Above 250 °C, we observed an entirely different spectrum, corresponding to a much higher muon hfc. Accordingly we suggested that this could be the Mu adduct of the enol, that is, the 1-Mu-2-hydroxy-2-propyl radical $CH_3C(OH)CH_2Mu$.[12] The μLCR results of the current study provide confirmation for this assignment.

Figure 6 contrasts the spectra obtained under conditions where the keto and enol adducts are detected. Proton hfc values were calculated from the resonance field positions and muon hfc values interpolated from the TF-μSR study.[12] The results are reported in Table 2. There is an obvious similarity between the spectrum shown in Figure 6b and those in Figures 2−5, and there can be little doubt that this is due to the presence of CH_3 and CH_2Mu groups in the radical.

It is interesting to note that H addition to the keto and enol forms of acetone gives only one product, 2-hydroxy-2-propyl; an isotope study is needed to distinguish the two reaction channels. Thus, the two radicals listed in Table 2 are isotopomers and differ only in the site of Mu substitution. The conformational effect of Mu substitution in the methyl group was discussed earlier in this paper, and this accounts for the difference in proton hyperfine couplings in CH_3 and CH_2Mu for the enol adduct. However, there is a significant difference between the unsubstituted CH_3 couplings of the two radicals. Unfortunately, it proved impossible to record μLCR spectra of the two radicals under the same conditions, because the resonance position for the keto adduct approaches zero field as the temperature is raised to the region where the enol adduct can be detected. One possible explanation for the different CH_3 couplings is that hydrogen bonding of the hydroxyl group to neighboring water molecules[3] serves to reduce the unpaired spin density on the 2-carbon, which would lower the hfc's of the β protons. A similar explanation has previously been advanced to explain temperature and solvent effects on the muon hfc in the 2-muoxy-2-propyl isomer.[24] In addition, there appears to be a large isotope effect on the dihedral angle between the OMu/OH group and the carbon plane.[24] Whether this also influences the methyl hfc is not clear. We plan to explore such questions by extending our studies to ^{13}C-labeled material. The additional level-crossing resonance due to ^{13}C in the 2-position should be accessible throughout the temperature range and allow us to study the enol and keto adducts under identical conditions.

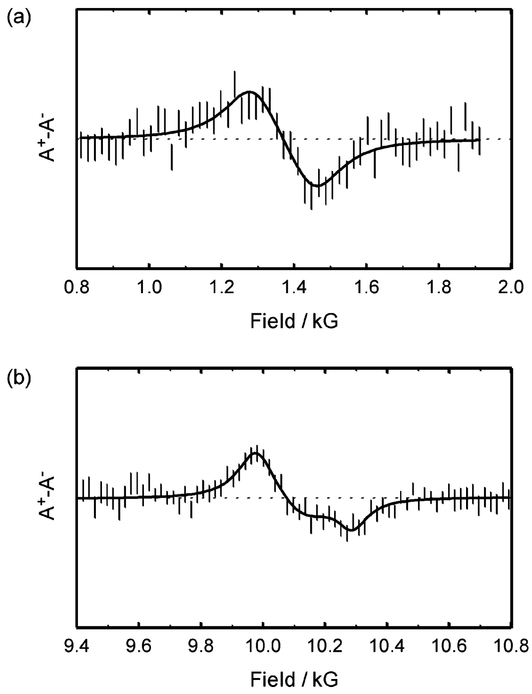

Figure 6. μLCR spectra of the muoniated radicals formed from (a) the keto form of acetone in water (0.5 M) at 92 °C, 136 bar; and (b) the enol form of acetone in water (0.6 M) at 350 °C, 250 bar.

Summary

Transient organic free radicals can be detected under hydrothermal conditions and unambiguously identified by their hyperfine constants as determined from a combination of transverse-field muon spin rotation and avoided-level crossing spectroscopy. The latter technique has the added advantage of permitting studies of dilute systems, where the pseudo-first-order rate constant for generation of the muoniated radical is as slow as 10^6 s^{-1}. The identities of the muoniated radicals formed in superheated aqueous solutions of alcohols are consistent with dehydration of the alcohols to alkenes with ease of conversion in the order tertiary > secondary > primary.

Two muoniated radicals are formed in aqueous solutions of acetone. At low temperatures, where the keto form is dominant,

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Mu adds to the carbonyl oxygen, but at higher temperatures, Mu adds to the terminal carbon of the enol. The radical products are both isotopomers of 2-hydroxy-2-propyl and differ only in the site of Mu substitution.

Muon spin spectroscopy is the only technique currently being used to characterize transient free radicals under hydrothermal conditions in an unambiguous manner.

Acknowledgment. We thank the staff of the Centre for Molecular and Materials Science at TRIUMF for technical support; in particular, Dr. D. J. Arseneau was responsible for developing the muon beam tunes with transverse and longitudinal spin polarization. This work was financially supported by Science and Engineering Research Canada (NSERC) and, through TRIUMF, by the National Research Council of Canada.

Supporting Information Available: Additional details of apparatus, including a schematic drawing of the pressure cell assembly. Equations used to calculate hyperfine constants from spectral features. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0537070